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SOLID FILM LUBRICANT DEVELOPMENT FOR AIR FORCE REQUIREMENTS

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AIR FORCE MATERIALS LABORATORY
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A STUDY OF HIGH TEMPERATURE CERAMIC ADHESIVES, DEVELOPED FOR METAL TO METAL BONDING IS DISCUSSED AS ONE EFFORT TO PROVIDE POTENTIAL BINDERS. COMPOSITION, FORMULATION TECHNIQUES, AND EVALUATION TESTS ARE DESCRIBED. EFFECTS OF PROPERTIES SUCH AS TERMAL EXPANSION IS ILLUSTRATED. ONE OF THE MORE PROMISING FORMULATIONS, CALCIUM FLUORIDE - CERAMIC ADHESIVE, WAS STUDIED IN DETAIL.

THE CONCLUSIONS DRAWN FROM THESE TESTS INDICATE THE CERAMIC ADHESIVES CAN BE USED AS BONDING AGENTS FOR HIGH TEMPERATURE LUBRICATING PIGMENTS AND DO PROVIDE LUBRICATION UNDER THE CONDITIONS TESTED.

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FOREWORD

This report was prepared by the Fluid and Lubricant Materials Branch of the Nonmetallic Materials Division. The work was initiated under Project Nr. 3044, "Aerospace Lubricants", Task Nr. 304404, "Dry Lubrication Development". The work was administered under the Air Force Materials Laboratory, Deputy Commander/Research & Engineering, Aeronautical Systems Division, with Bobby D. McConnell acting as project engineer.

ABSTRACT

General Air Force requirements for lubricating system which will operate under a wide range of extreme environmental conditions are outlined. Current research and development programs are briefly reviewed in terms of the types of effort being conducted to meet these requirements.

A study of high temperature ceramic adhesives, developed for metal to metal bonding is discussed as one effort to provide potential binders. Composition, formulation techniques, and evaluation tests are described. Effects of properties such as thermal expension is illustrated. One of the more promising formulations, calcium fluoride - ceramic adhesive, was studied in detail at temperatures from 200° F to 1,400° F, 216 ft/min sliding speeds and 61 pound normal load. Friction coefficients ranged from .13 to .38. The conclusions drawn from these tests indicate the ceramic adhesives can be used as bonding agents for high temperature lubricating pigments and do provide lubrication under the conditions tested.

This report has been reviewed and is approved.

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INTRODUCTION

This paper will briefly outline some of the present and anticipated future lubrication requirements of aerospace vehicles and briefly discuss some of the programs of the overall effort to develop lubricating media to meet the extreme environmental conditions brought about by these advanced vehicles.

The development of more advanced and increasingly complex aircraft, missile, and other weapon systems has brought about requirements for lubricants which exceed the capabilities of lubricants currently in use. These requirements include operation at high temperatures in both oxidizing (air) environments and vacuums (10^{-6} Torr).

The discussion which follows is essentially divided into three parts. The first covers general requirements for present weapon systems and the anticipated requirements for future systems. The second part describes some of the Air Force's contractual programs which are designed to meet these requirements. The third area is a more detailed discussion of an internal Air Force effort to investigate the use of high temperature ceramic adhesives as bonding agents for high temperature solid film formulations.

Solid Film Lubrication Requirements for Present and Future Air Force Systems

Solid film lubricants are currently in wide use in various systems with applications being found in slow sliding bearings operating under loads up to 100,000 PSI in the temperature range of ambient to 500°F. These applications include lubrication in areas which are practically impossible to lubricate with the conventional systems. Examples of these applications include lubrication of the rod-end stablizing link assembly and eleven assembly on the B-58 aircraft. Flap Hinge pins and aileron Hinge pins on the F-104 aircraft are coated prior to enitial assembly of the part. Operation for the life of the part, without the necessary relubrication or maintenance, is a goal sought through the use of solid

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film lubricants.

The development of mach 3 aircraft such as the RS-70 and Supersonic Transport has pushed the lubricating requirements toward the 1000°F range. For example, some of the servo and hydraulic actuators call for operation up to 700°F and 50,000 PSI for 500 hours. Compressor inlet temperatures of 600°F and discharge temperatures of 1200°F will require lubricating systems to operate somewhere between these two temperatures. After burner sections of jet engines are seeing temperatures to 1800°F and any moving part should be adequately lubricated to insure reliable operation.

Advanced systems will bring additional lubrication requirements in addition to high temperatures. This is the requirement of lubrication in the vacuum of space as well as the high temperature, oxidizing environments encountered during reentry. The temperatures generated during reentry are expected to be as high as 1800° to 2000°F for short periods of time. The development of a lubricating system to provide adequate lubrication in both vacuum and oxidizing environments in the temperature range of ambient to 2000°F is one of the most challenging to the lubrication industry today.

Lubrication of satellites and other space systems, while not necessarily requiring extremely high temperature lubrication, do require lubricants that will operate at pressures of 10^{-10} Torr or lower for very long periods of time. Most liquid and grease lubricants contain components which are too volatile to operate successfully under these conditions. Solid film lubricants are being fully exploited for such uses primarily because they appear to offer the most feasible means of lubrication under these conditions.

These requirements are expected to increase at both ends of the scale as future systems come into being. Table 1 depicts and summarizes these trends. Temperatures will range from cryogenic to 2500°F. Loads can be expected from

TABLE 1

PRESENT AND FUTURE ANTICIPATED LUBRICATION REQUIREMENTS

FOR AIR FORCE WEAPON SYSTEMS

	Present Requirements	Future Anticipated Requirements
Temperature	$-300^{o}F$ to $1500^{o}F$	$-450^{o}F$ to $2500^{o}F$
Pressure	Atmospheric to 10^{-6}Torr	Atmospheric to 10^{-13}Torr
Loads	Zero to 100,000 psi	Zero to 200,000 psi
Speeds	1 to 10,000 rpm	1 to 100,000 rpm
Duration	up to 500 hours	to 30,000 hours

zero to above 200,000 PSI. Lubrication for life may be realized as time is extended from a few hundred hours to 30,000 hours or roughly three years. Pressures will range from atmospheric to inter lunar (10^{-13} torr) and possibly interplanetary (10^{-16} torr). Speeds will range from a few revolutions per hour to over 100,000 rpm. Other requirements may be generated as more complex systems are developed and other extreme environments are encountered. It is the goal of lubrication research and development to keep the state-of-the-art in lubricants and lubricating systems for these extreme environments well ahead of the time when the hardware becomes operational. The discussion below will describe some of the Air Force's research and development in solid film lubricants.

Current Air Force Programs in Solid Film Lubricants

In order to better understand the mechanisms of lubrication and advance the state-of-the-art in solid lubricating materials, a number of programs have been actively pursued by the Air Force. These programs and their data will not be discussed in detail during the Conference, therefore they will be described briefly here as to their direction and progress.

The first is a program conducted at Midwest Research Institute in which the basic crystal properties of a solid lubricant are studied. The study is concentrated primarily on single crystals of graphite and is pointed towards achieving a greater understanding of the basic lubrication mechanisms of lamellar solids and determining which of these mechanisms exercise influence over the lubricating properties of lamellar solids. This work is carried out in an ultra high vacuum system which is capable of maintaining pressures below 10^{-13} Torr (1). Work conducted to date has consisted of measuring the cohesive energy between layers of mica and graphite. The work was conducted with mica first to develop the handling and mounting techniques involved with the small crystals as well to refine the data for the cohesive energy of mica that has been reported earlier (2). The data gathered for mica indicate that there is a thirty (30) fold increase in the energy required to separate the layers in vacuum (10^{-13}Torr) as in air (3). Also, in studying the effects of contaminating gases on this energy, helium, argon, and nitrogen had no effect on the cohesive energy. However, water vapor at a pressure of 10^{-1} Torr will cause rapid separation of the layers. Additional tests are to be conducted with oxygen and hydrogen, and the entire series repeated with the graphite single crystals. Preliminary studies with graphite indicate the energy to separate the layers in vacuum is greater than the yield strength of the crystal and that the crystals will have to be strengthened before the cohesive energy measurements can be made. This work is continuing.

Another program designed to investigate the mechanisms involved in solid film lubricating systems is being conducted at the University of Illinois, Ceramic Engineering Department. This program is to study the reactions, phase changes, etc. which take place in a ceramic bonded solid film lubricant at different temperatures. This work began with a study of the PbS-B_2O_3 system which had excellent lubricating properties at $1000^{\circ}F$ but dropped off sharply at $800^{\circ}F$. The work to date indicates that the binder plays a very important role in the frictional behavior of the system. The B_2O_3 was found to primarily govern the frictional and lubricating behavior in the PbS-B_2O_3 system (4). Other systems using the B_2O_3 as the binder are being studied to enable a greater understanding of the part played by the binder in the ceramic bonded systems. The data gathered in this program will allow selection of materials with the specific properties needed to formulate superior high temperature solid film lubricants. This work is continuing.

The third program, which has just started, is an effort designed to enhance the successful development of high temperature solid film lubricants with the capability of operating over a wide range of environmental conditions. This program constitutes a broadening of the overall effort in the development of solid films in that a number of different approaches in bonding techniques are being studied. These techniques include vacuum deposition, flame spraying, chemical bonding, specific ceramic materials, as well as other promising techniques which may become available. The various techniques are being developed by organizations known to be competent in the particular area and the resulting formulations forwarded to the prime contractor for final evaluation of friction, wear, and lubrication properties. The most promising techniques will be further developed to provide solid film lubricants with operational capability over a range of environmental conditions.

CERAMIC ADHESIVES AS SOLID FILM BINDERS

The final solid film development program to be discussed is an internal Air Force effort conducted within the Nonmetallic Materials Laboratory. This effort was concerned with the investigation of high temperature ceramic materials as potential bonding agents for high temperature lubricating pigments.

Ceramic materials as binders for solid film lubricating systems have been extensively investigated. However, there are materials available which have specific properties built into them and which could give far different results than the single component materials which have been studied in the past. Some of the properties such as ductility, shear strength, viscosity, thermal expansion and curing temperature have been largely ignored in the selection of materials as bonding agents. There is a general class of ceramic materials which have been studied extensively in which much consideration was given to these properties. They are the high temperature, inorganic, ceramic adhesives developed especially for metal to metal bonding (5). Some of these adhesives possess properties which make them attractive for study as bonding agents. The wide interest in solid lubricants and the great variety of properties of these adhesives make additional research necessary on such ceramic materials.

Two (2) adhesives were studied initially in this program. Table 2 gives the code designation and composition of the ceramic adhesives investigated. These adhesives were selected because of the background data available and properties exhibited by each composition. It was felt that the compositions were different enough, primarily in the metal oxides, to give a difference in results as binders. Both adhesives were already ground to 200 mesh and were used in the formulations without further grinding or milling.

Compatibility - Adhesive Versus Substrates

One of the first things noted and studied in these tests was the compatibility of the pure adhesive materials and the bearing substrate on which they were coated. A practice of observing the coatings on the test specimens after curing was established to give an indication of the type of surface the coating had formed and the extent of oxidation of the metal test specimens. The instrument used for these observations was an AO Spencer Cycloptic Microscope with magnification from 10 to 40 X.

It was noted that in some of the coatings observed, that cracking or crazing was occurring within the film. The cracks appeared to be at the interface between the metal surface and the coating. It was felt that the probable cause was in coefficent of thermal expansion of the substrate and the adhesive. This was verified by observing the coating on some test specimens as they cooled to ambient temperature after curing. When they approached the lower temperatures the cracks would begin to appear and in some cases would continue until the entire surface was covered. Figures I and II compare the surface of cracked and uncracked coatings. It was felt that this cracking would definitely affect the wear life of the film, and rather than go into a detailed study involving coefficients of expansion, etc., a series of tests were conducted to indicate which were compatible. Test specimens of the different metals available were coated with the pure adhesives, fired

TABLE 2

CERAMIC ADHESIVE COMPOSITION

Adhesive Code	Composition (Parts by Weight)
A-2	SiO_2 - 37.2
	Na_2O - 4.9
	B_2O_3 - 55.9
	Fe_2O_3 - 2.0
A-3	Al_2O_3 - 0.98
	BaO - 44.01
	B_2O_3 - 6.50
	CaO - 3.53
	SiO_2 - 37.72
	ZnO - 5.00
	ZrO_2 - 2.26

at the curing temperature, allowed to cool, and checked with the microscope for cracking. Table 3 shows the combinations of test specimens and adhesives studied. As shown, only the Inconel-X and Rene' 41 metals did not show the crazing or cracking with the ceramic materials tested. Therefore for any further testing only Inconel-X or Rene' 41 test specimens should be used for these formulations.

Adhesive Formulations

The preparation procedure used for these formulations consisted of the following:

The lubricating pigment and adhesive were weighted to the nearest 0.1 gram as dry powders and mixed in the various ratios indicated. This mixture was placed in a small spraying jar and enough water added to make an easy flowing slurry. The jar was placed on a magnetic stirrer and allowed to mix well while the test specimens were prepared. The test specimens were placed in petroleum ether to remove the protective oil film, scrubed and wiped clean, and placed in acetone until ready for use. The test specimens were pre-oxidized at the curing temperature of the adhesive - 1700°F for five (5) minutes to provide a thin oxide layer which has been reported to enhance the adherence of the ceramic materials to the substrate (6). After pre-oxidizing, they were removed and immediately transferred to the spray booth and placed on the rotating shaft. The specimens were rotated at a slow speed and sprayed as soon as they cooled enough for the slurry to adhere. The spray gun was adjusted to spray a fine, even mist and the coating built up to the desired thickness by successive passes of the spray across the face of the specimens. The slurry was constantly agitated by the magnetic stirrer during the operation to insure a uniform mixture of pigment and adhesive. When the desired thickness was obtained, the test specimens were allowed to air dry and then placed in the furnace at 1700°F for five (5) minutes. After curing, they were removed, allowed to cool, and then were ready for the friction and wear tests.

TABLE 3

COMPATIBILITY - SUBSTRATE VS ADHESIVES

Test Specimen	Adhesive	Pre-Oxidized	Results
Rex AAA	A-2	Yes	Film Spotty, crazing, Poor adherence
Rex AAA	A-1	No	Crazing
Inconel-X	A-1	Yes	Film smooth and uniform, good adherence
Inconel-X	A-2	Yes	Film smooth, good adherence
440 SS	A-2	Yes	Film smooth, crazing
440 SS	A-1	Yes	Film smooth, crazing
M-10	A-2	Yes	Film rough
Rene' 41	A-2	Yes	Film smooth and uniform, good adherence, no crazing
Rene' 41	A-1	Yes	Film smooth and uniform, good adherence, no crazing

The many screening tests involving various formulations and compositions will not be discussed here. These tests are described in more detail in a recent ASD report (7). A number of lubricating pigments including MoS_2, PbO, and the fluoride salts of Calcium, Barium, Lithium and Chromium were tried in various ratios with varying results.

The only formulation considered worthy of further study was the CaF_2 -A-2 system in a lubricant to binder ratio of 4 to 1. This ratio is similar to the one (3 to 1) reported by NASA in their study of a ceramic bonded calcium fluoride film (6). The binder used by NASA in these studies was formulated specifically for this pigment and the nickel base alloy substrates. The binder was formulated on the basis of softening range, vitrifying tendency, and thermal expansion properties and points out the success obtained in formulating the binder for the particular lubricating system, i.e., pigment and substrate.

For the detailed study of the CaF_2 -A-2 system, twenty-four (24) Rene' 41 test specimens were prepared and coated from the same formulation batch. The test specimens were sprayed in groups of four (4) at the same time and by the same person to reduce the variables of preparation. An investigation of the wear life capability of this formulation in the 200° to 1400°F at range two levels of speed and load was attempted. Only the high speed, light load, (600 rpm, 61 pound load) gave reasonable results. Attempts to conduct tests at high load and low speed were futile because of the high friction, wear, vibration, etc. This same effect has been noted by other investigators conducting tests at low speeds and high loads with ceramic bonded films, and they feel that these films require conditions that produce high interfacial temperature when sliding to give good performance. Table 4 shows the results of the high speed low load tests conducted at the various temperatures. Figure III shows the data as they appear as average wear life versus temperature. Failure of the film was estimated as close as possible to the break-

TABLE 4

DATA FOR THE C_eF_2-A-2 SYSTEM AT 600 RPM, 61 POUND LOAD ON RENE' 41

Temp (^oF)	Scar Width (.in)	Wt. Loss	Coefficient of Friction	Wear Life
1000	.154	.016	.22	21,000
1000	.114	.005	.17	18,000
500	.156	.013	.37	12,000
1400	.210	.008	.19	17,885
750	.132	.012	.32	12,000
1200	.132	.088	.27	15,000
1200	.126	.007	.13	19,000
750	.080	.002	.29	12,500
200	.071	.004	.35	1,332
500	.071	.002	.34	7,000
200	.049	.001	.38	1,258

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through and rise in friction. The curve in Figure III indicates a possible decrease in wear life above 1200°F but is not conclusive because of the inability to obtain test results at temperatures above 1400°F due to heater limitation. The one point at 1400°F is questionable because of this and could not be verified because of heater failure on the attempted check runs.

Conclusions

The above test indicate the possibility of obtaining some formulations of high temperature ceramic adhesives and lubricating pigments which may have potentiality as a solid film lubricant under the conditions tested. There is evidence to indicate that better bonding is obtained with these adhesives when the substrate is pre-oxidized to allow formation of an oxide layer. While no specific measurements were made in this study, the data also indicate that the coefficient of thermal expansion of the substrate and ceramic binder must be closely matched to obtain a good adhering film. These tests also point out that oxidative stability of the lubricating pigment is very important in formulations for high temperature use, and that the pigment should be selected to fit into the range being investigated. These ceramic adhesives behave as other ceramic binders have, that is low friction and wear occurs at the higher temperatures but higher friction and wear and much shorter wear life occurs in the lower temperature ranges (ambient to 800°F). It is felt that difficulties would be encountered in attempting to formulate high temperature solid film lubricants for wide temperature ranges using these ceramic adhesives as binders, however certain formulations are feasible for specific applications through proper selection of lubricating pigments and binders. This would entail operation in a narrow temperature range with selection of a lubricating pigment which exhibited it's best performance in this range. Also the binder would be selected on the basis of its compatibility with the pigment and substrate from the standpoint of coefficient of thermal expansion. It is generally considered that greater success is obtained in attempting to formulate solid film lubricants for a specific application in which the operating parameters are clearly defined, than to attempt formulations which cover a wide range of environmental conditions.

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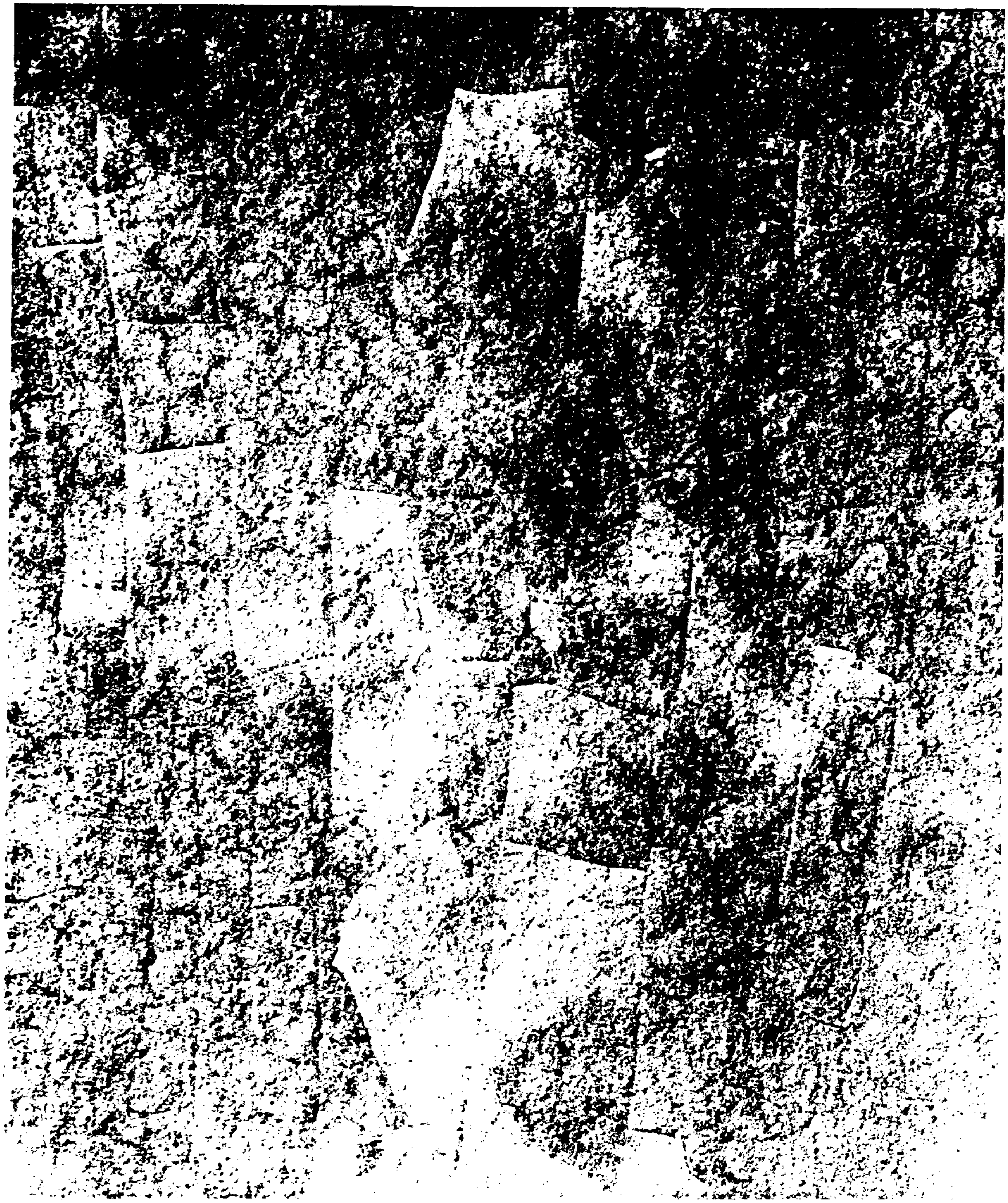

FIGURE I. CRACKED COATING ON 440 SS

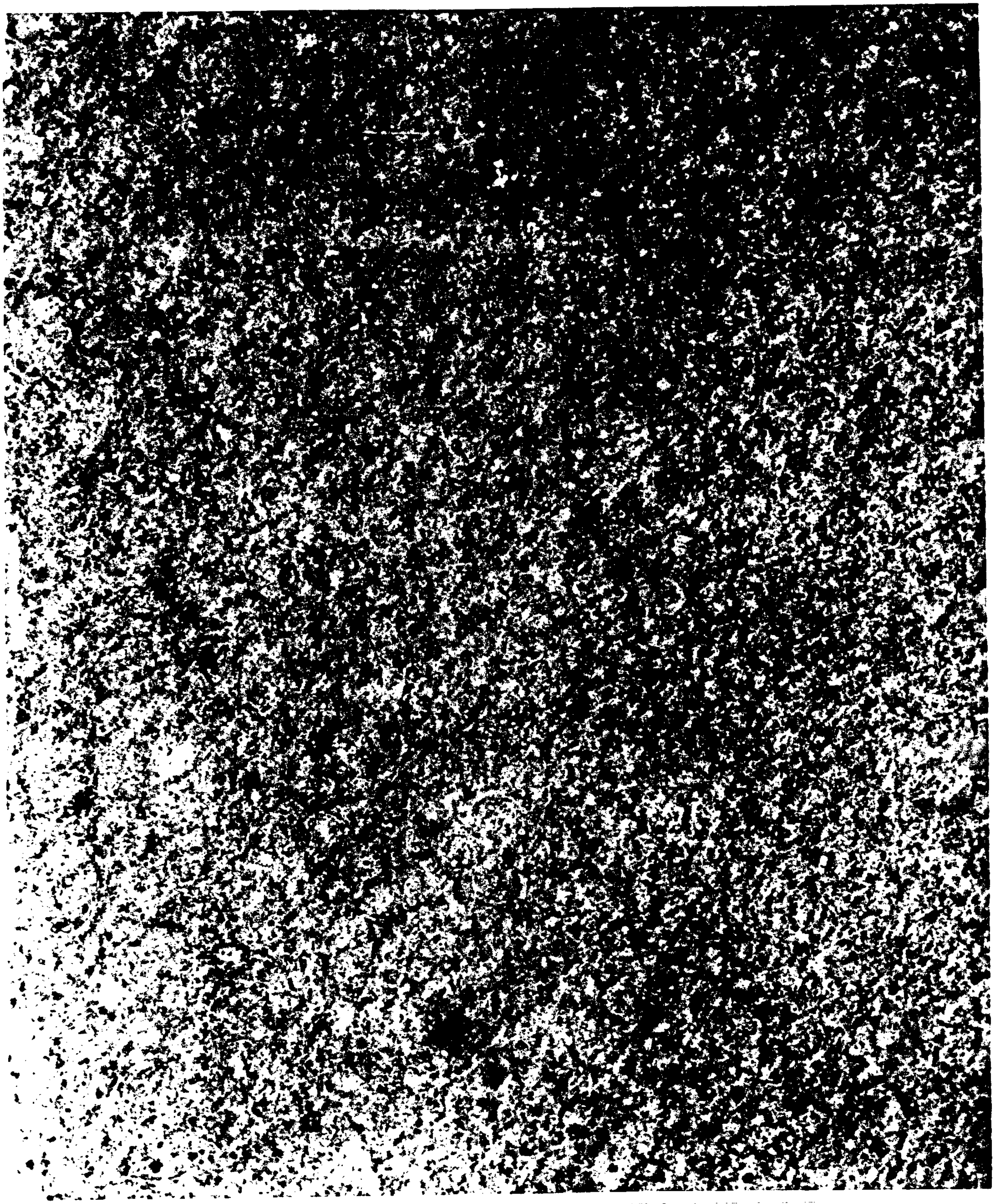

FIGURE 2. UNCRACKED COATING ON INCONEL X

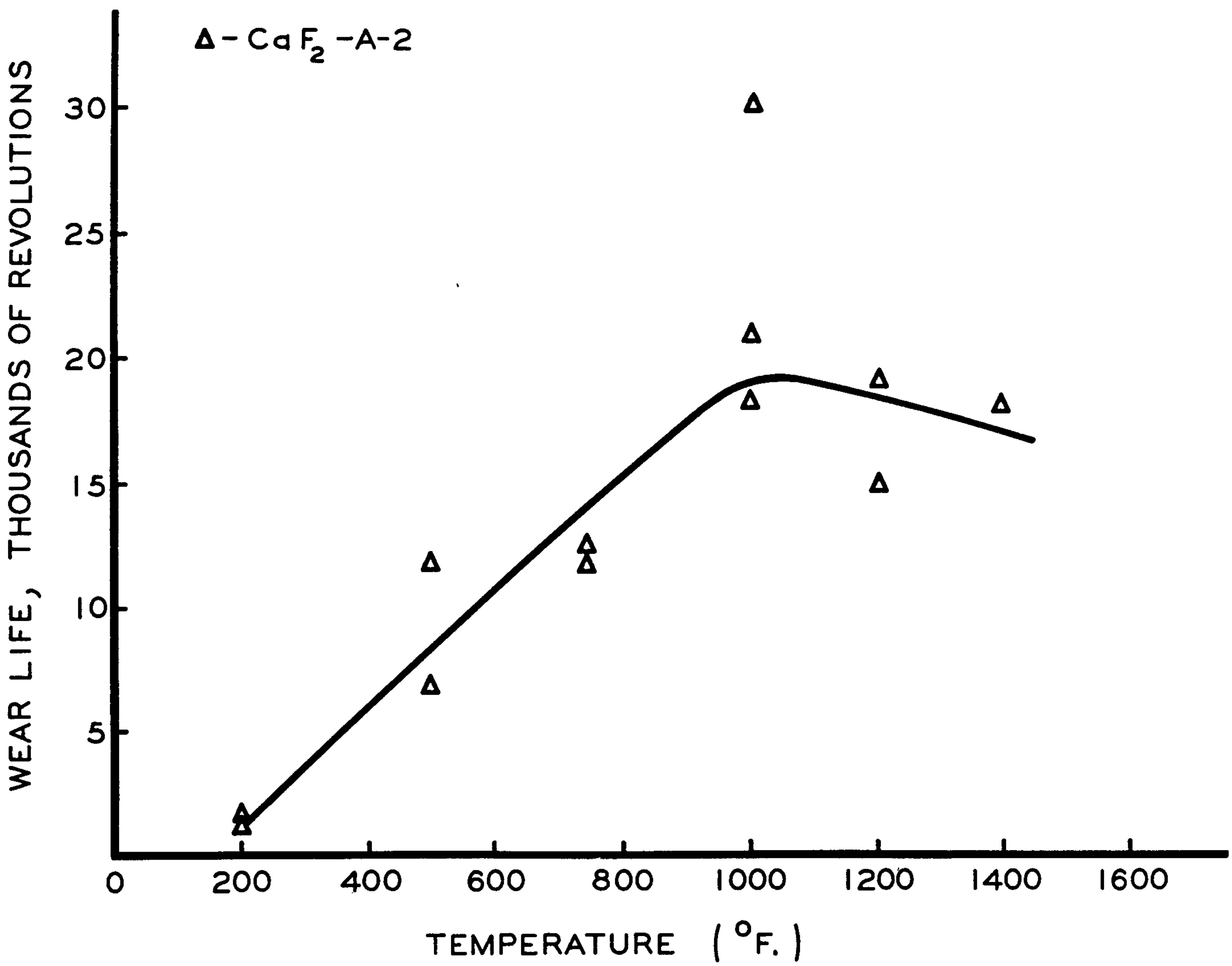

FIGURE 3. WEAR LIFE VS TEMPERATURE